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(54) Wasch- und Reinigungsmittel.

(57) Das Wasch- und Reinigungsmittel der Erfindung mit 5–70 Gew.% mindestens eines Tensids, 0,1–50 Gew.% mindestens eines Gerüststoffes sowie üblichen Waschhilfsmitteln ist durch folgende Gerüststoffgehalte gekennzeichnet:

a) 0,1–25 Gew.% eines Copolymers, erhältlich durch an sich bekannte Copolymerisation folgender Monomere:

aa) 40–99,9 Mol-% ethylenisch ungesättigter Carbonsäuren oder deren Alkalisalze der allgemeinen Formel
$R^1(R^2)C=C(R^3)COOX$,
worin X = H, Alkalimetall;
R^2 = H, COOX, C_1–C_4-Alkyl, C_5–C_8-Cycloalkyl, Phenyl oder substituiertes Phenyl;
R^1, R^3 = H, C_1–C_4-Alkyl, C_5–C_8-Cycloalkyl, Phenyl, substituiertes Phenyl bedeuten.
oder deren Anhydride;

bb) 0,1–40 Mol-% ethylenisch ungesättigter Phosphonsäuren oder deren Alkalisalze der allgemeinen Formel
$R^4(R^5)C=C(R^6)PO_3X_2$,
worin X = H, Alkalimetall;
R^4, R^5 = H, C_1–C_4-Alkyl, C_5–C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;
R^6 = C_1–C_4-Alkyl, C_5–C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;

cc) 0–20 Mol-% olefinisch ungesättigte Verbindungen ohne Carbon- oder Phosphonsäuregruppen.

b) 0–49,9 Gew.% übliche Gerüststoffe.

Die Erfindung betrifft weiterhin die Verwendung des Copolymers als Gerüststoff oder Gerüststoffadditiv in Wasch- und Reinigungsmitteln.

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HOECHST AKTIENGESELLSCHAFT

Wasch- und Reinigungsmittel

Ein für den Wascherfolg von Wasch- und Reinigungsmitteln entscheidender Waschmittelinhaltsstoff ist das Pentanatriumtriphosphat, $Na_5P_3O_{10}$, technisch auch Natriumtripolyphosphat, NTPP, genannt. Die Verbindung verfügt über folgende wirksame Eigenschaften:

- Komplexierung von Erdalkaliionen,
- selektive Adsorption an Grenzflächen von Textilsubstrat und Schmutz,
- Verstärkung der Wirkung von Anion-Tensiden,
- Dispergierung von Pigmentschmutz,
- Alkalische Reaktion,
- Pufferwirkung,
- "Threshold"-Wirkung,
- Gerüstsubstanz für Wasch- und Reinigungsmittel.

Von besonderer Bedeutung für die Reinigungsleistung heutiger Waschmittel sind dabei das Calciumbindevermögen, die Dispergierwirkung sowie der "Threshold"-effekt, worunter man die Eigenschaft einer Substanz, im unterstöchiometrischen Einsatz die Ausfällung von Härtebildnern zu verzögern bzw. zu verhindern, versteht.

Ein unerwünschter Nebeneffekt von NTPP ist, daß es - neben Phosphaten aus anderen Quellen, wie Düngemitteln, Fäkalien, Bodenerosion u.a.m. - zum Phosphoreintrag in die Gewässer beiträgt. Überhöhte Phosphorkonzentrationen, besonders in stehenden und langsam fließenden Gewässern, können zu Eutrophierungserscheinungen führen.

Aus diesem Grund sucht man seit langem nach vergleichbar gut geeigneten Phosphatersatzstoffen. In verschiedenen Ländern wurden behördliche Schritte unternommen, um den Einsatz von NTPP in Waschmitteln einzuschränken bzw. ganz zu verbieten. In der Bundesrepublik Deutschland führte die Phosphatverminderung bei den Waschmitteln zu schlechteren Waschergebnissen. Insbesondere wurden erhöhte anorganische Gewebeinkrustierungen beobachtet; zweifelsohne beeinträchtigt eine zu hohe Gewebe-Inkrustierung die Gebrauchseigenschaften des Waschgutes.

Es bestand also die Aufgabe, Phosphatersatzstoffe zu finden, die die Wirkung des Gerüststoffsystems und damit die Wirkung des Waschmittels wieder verbessern.

Es sind viele Substanzen als völliger oder teilweiser NTPP-Ersatz diskutiert worden, z.B. Zeolith A, Trinatriumnitrilotriacetat und Natriumcitrat. Aus verschiedenen Gründen - z.T. ökologische Bedenken, mangelnde Wirtschaftlichkeit, nicht in jeder Beziehung befriedigende Leistungsfähigkeit - ist bisher keine Substanz gefunden worden, die sich allein als NTPP-Substitut durchsetzen konnte. Vielmehr ist zunehmend die Meinung vertreten worden, daß Kombinationen von Gerüststoffen bzw. Gerüststoffadditiven optimale Leistungsfähigkeit erbringen können. Als Gerüststoffadditive sind dabei Verbindungen zu bezeichnen, die in relativ kleinen Anwendungskonzentrationen merklichen Einfluß auf das Gerüststoffsystem ausüben.

Die Erfindung betrifft ein Wasch- und Reinigungsmittel mit 5 bis 70 Gew% mindestens eines Tensids, 0,1 bis 50 Gew% mindestens eines Gerüststoffes sowie üblichen Waschhilfsstoffen, welches gekennzeichnet ist durch folgende Gerüststoffgehalte:

a) 0,1 bis 25 Gew% eines Copolymers, erhältlich durch an sich bekannte Copolymerisation folgender Monomere:

aa) 40 bis 99,9 Mol% ethylenisch ungesättigter Carbonsäuren oder deren Alkalisalze der allgemeinen Formel $R^1(R^2)C=C(R^3)COOX$,
worin X = H, Alkalimetall;
R^2= H, COOX, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl oder substituiertes Phenyl;
R^1, R^3 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl bedeuten,
oder deren Anhydride;

bb) 0,1 bis 40 Mol% ethylenisch ungesättigter Phosphonsäuren oder deren Alkalisalze der allgemeinen Formel
$R^4(R^5)C=C(R^6)PO_3X_2$,
worin X = H, Alkalimetall;
R^4, R^5 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;
R^6 = C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;

cc) 0-20 Mol% olefinisch ungesättigte Verbindungen ohne Carbon- oder Phosphonsäuregruppen.

b) 0 bis 49,9 Gew% übliche Gerüststoffe.

Die Erfindung betrifft ebenso die Verwendung eines Copolymers, erhältlich durch an sich bekannte Copolymerisation folgender Monomere:

a) 40 bis 99,9 Mol% ethylenisch ungesättigter Carbonsäuren oder deren Alkalisalze der allgemeinen Formel
$R^1(R^2)C= C(R^3)COOX$,
worin X = H, Alkalimetall;
R^2 = H, COOX, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl oder substituiertes Phenyl;
R^1, R^3 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl bedeuten
oder deren Anhydride;

b) 0,1 bis 40 Mol% ethylenisch ungesättigter Phosphonsäuren oder deren Alkalisalze der allgemeinen Formel

$R^4(R^5)C=C(R^6)PO_3X_2$,

worin X = H, Alkalimetall;

R^4, R^5 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;

R^6 = C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;

c) 0-20 Mol% olefinisch ungesättigte Verbindungen ohne Carbon- oder Phosphonsäuregruppen;

als Gerüststoff oder Gerüststoffadditiv in Wasch- und Reinigungsmitteln.

Vorzugsweise werden 65 bis 98 Mol% ethylenisch ungesättigte Carbonsäuren, 2 bis 30 Mol% ethylenisch ungesättigte Phosphonsäuren und 0 bis 5 Mol% andere olefinisch ungesättigte Verbindungen zu den erfindungsgemäß eingesetzten Copolymeren polymerisiert. Diese Copolymeren der Erfindung werden als Gerüststoffe bzw. Gerüststoffadditive bevorzugt zusammen mit Pentanatriumtriphosphat, Zeolith A oder Trinatriumnitrilotriacetat als weiteren Gerüststoffen in die Wasch- und Reinigungsmittel eingearbeitet.

Zur Darstellung der Copolymere werden als ethylenisch ungesättigte Carbonsäuren bzw. als deren Anhydride bevorzugt Acrylsäure, Methacrylsäure, Vinylessigsäure oder Maleinsäureanhydrid, als ethylenisch ungesättigte Phosphonsäuren bevorzugt 1-Phenylvinyl-1-phosphonsäure oder Propen-2-phosphonsäure eingesetzt. Die Copolymerisierung anderer olefinisch ungesättigter Verbindungen ohne Carbon- oder Phosphonsäuregruppen ist nicht erforderlich, doch können z.B. Ethylen, Butadien, Chloropren, Acrylamid, Methacrylamid, Acrylamidosulfonsäure, Vinylsulfonsäure, Allylsulfonsäure, Vinylacetat, Hydroxyethyl- oder -propylacrylat, Vinylglykol oder (Meth) acrylsäuremethylester mit einpolymerisiert werden.

Die erfindungsgemäß als Gerüststoff fungierenden Copolymere weisen zugleich den Charakter polymerer Carbonsäuren und von Phosphonsäuren auf und entfalten ihre hervorragenden inkrustierungsinhibierenden und dispergierenden Eigenschaften mit verschiedenen Gerüststoffsystemen gleichermaßen, z.B. in Kombination mit NTPP und Zeolith A.
Die monomeren ethylenisch ungesättigten Carbonsäuren sind im allgemeinen großtechnisch verfügbare Produkte; die monomeren ethylenisch ungesättigten Phosphonsäuren sind in einfacher und wirtschaftlicher Weise z.B. durch Umsetzung von Ketonen mit Phosphortrichlorid (DE-OS 33 23 392) oder mit Tetraphosphorhexoxid (DE-OS 31 25 329 und DE-OS 32 10 419) erhältlich.

Die DE-OS 18 01 411 beschreibt die Verwendung von wasserlöslichen Salzen organischer Polymerverbindungen, die Phosphon- und Carbonsäuregruppen in den Seitenketten enthalten, als alleinige Gerüststoffe in Wasch- und Reinigungsmitteln. Als Phosphonsäuremonomer dient dabei die Vinylphosphonsäure. Die alleinige Anwendung dieser Gerüststoffe ist jedoch wirtschaftlich nicht durchführbar.

Die Herstellung der erfindungsgemäß als Gerüststoff fungierenden Copolymere aus den genannten Monomeren durch radikalische Polymerisation ist an sich bekannt oder kann nach vergleichbaren Vorschriften durchgeführt werden (vgl. z.B. DE-OS 24 55 624, Beispiel 10; DE-OS 18 01 411, Seite 5).

Die erfindungsgemäß in den Wasch- und Reinigungsmitteln enthaltenen Gerüststoffe können in üblicher Weise durch Sprühtrocknen, Mischen oder Sprühnebelmischverfahren in die Wasch- und Reinigungsmittel eingearbeitet werden. Ein weiterer Vorteil der Gerüststoffe bzw. Gerüststoffadditive gemäß der Erfindung ist ihr Beitrag zum "anti-caking", d.h. zur Verhinderung von Entmischungserscheinungen in Waschmittelslurries, die reich an nicht-ionischen Tensiden sind.

Die erfindungsgemäßen Wasch- und Reinigungsmittel zeichnen sich durch hervorragende Waschergebnisse aus. Sie haben ein ausgesprochen hohes Calciumbindevermögen sowie ausgezeichnete Dispergier- und Thresholdwirkung, so daß man ihnen neben der inkrustierungsinhibierenden Wirkung deutliche vergrauungsinhibierende Eigenschaften zuschreiben muß.

Das Wasch- und Reinigungsmittel der Erfindung enthält als Tenside bevorzugt solche anionischer, zwitterionischer (ampholytischer) oder nichtionischer Natur.

Unter anionischen Tensiden sind die wasserlöslichen Salze höherer Fettsäuren oder Harzsäuren, wie Natrium- oder Kaliumseifen von Kokos-, Palmkern- oder Rüböl sowie von Talg und Gemischen davon zu verstehen. Weiterhin zählen dazu höhere alkylsubstituierte, aromatische Sulfonate, wie Alkylbenzolsulfonate mit 9 bis 14 C-Atomen im Alkylrest, Alkylnaphthalinsulfonate, Alkyltoluolsulfonate, Alkylxylolsulfonate oder Alkylphenolsulfonate; Fettalkoholsulfonate ($R-CH_2-O-SO_3Na$; $R = C_{11-17}$) oder Fettalkoholethersulfate, wie Alkalilaurylsulfat oder Alkalihexadecylsulfat, Triethanolaminlaurylsulfat, Natrium- oder Kaliumoleylsulfat, Natrium- oder Kaliumsalze von mit 2 bis 6 Mol Ethylenoxid ethoxyliertem Laurylsulfat. Weitere geeignete anionische Tenside sind sekundäre lineare Alkansulfonate sowie α-Olefinsulfonate mit einer Kettenlänge von 12-20 C-Atomen.

Unter nichtionischen Tensiden sind solche Verbindungen zu verstehen, die eine organische, hydrophobe Gruppe sowie einen hydrophilen Rest aufweisen, z.B. die Kondensationsprodukte von Alkylphenolen oder höheren Fettalkoholen mit Ethylenoxid, die Kondensationsprodukte von Polypropylenglykol mit Ethylenoxid oder Propylenoxid, die Kondensationsprodukte von Ethylenoxid mit dem Reaktionsprodukt aus Ethylendiamin und Propylenoxid, sowie langkettige tertiäre Aminoxide ($C_{12}H_{25}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}=O$).

Schließlich umfassen Tenside mit zwitterionischem (ampholytischen) Charakter folgende Verbindungen:
Derivate von aliphatischen, sekundären und tertiären Aminen oder quaternären Ammoniumverbindungen mit 8 bis 18 C-Atomen und einer hydrophilen Gruppe im aliphatischen Rest, wie z.B. Natrium-3-dodecylaminopropionat, Natrium-3-dodecylaminopropansulfonat, 3-(N,N-Dimethyl-N-hexadecyl-amino)-propan-1-sulfonat oder Fettsäureaminoalkyl-N,N-dimethylacetobetain, wobei die Fettsäure 8 bis 18 C-Atome und der Alkylrest 1-3 C-Atome enthält.

Als Gerüstsubstanzen für die Waschmittel gemäß der Erfindung eignen sich schwach sauer, neutral oder alkalisch reagierende anorganische oder organische Salze, insbesondere anorganische oder organische Komplexbildner.

Brauchbare, schwach sauer, neutral oder alkalisch reagierende Salze sind beispielsweise die Bicarbonate, Carbonate oder Silikate der Alkalien, weiterhin Mono-, Di- oder Trialkaliorthophosphate. Di- oder Tetraalkalipyrophosphate, als Komplexbildner bekannte Metaphosphate, Alkalisulfate sowie die Alkalisalze von organischen,nicht kapillaraktiven, 1 bis 8 C-Atome enthaltenden Sulfonsäuren, Carbonsäuren und Sulfocarbonsäuren. Hierzu gehören beispielsweise wasserlösliche Salze der Benzol-, Toluol- oder Xylolsulfonsäure, wasserlösliche Salze der Sulfoessigsäure, Sulfobenzoesäure oder Salze von Sulfodicarbonsäuren sowie die Salze der Essigsäure, Milchsäure, Zitronensäure, Weinsäure, Oxydiessigsäure ($HOOC-CH_2-O-CH_2-COOH$), Oxydibernsteinsäure, 1,2,3,4-Cyclopentantetracarbonsäure, Polyacrylsäure und Polymaleinsäure.

Als komplexbildende Gerüstsubstanzen eignen sich auch die schwach sauer reagierenden Metaphosphate sowie die alkalisch reagierenden Polyphosphate, insbesondere das Tripolyphosphat. Sie können ganz oder teilweise durch organische Komplexbildner ersetzt werden. Zu den organischen Komplexbildnern gehören beispielsweise Nitrilotriessigsäure, Ethylendiamintetra-

essigsäure, N-Hydroxyethylethylendiamintriessigsäure, Polyalkylen-polyamin-N-polycarbonsäuren und andere bekannte organische Komplexbildner, wobei auch Kombinationen verschiedener Komplexbildner eingesetzt werden können.

Waschhilfsstoffe gemäß der Erfindung umfassen Produkte wie die Alkali- oder Ammoniumsalze der Schwefelsäure, Kieselsäure, Kohlensäure, Borsäure, Alkylen-, Hydroxyalkylen- oder Aminoalkylenphosphonsäure sowie Bleichmittel, Stabilisatoren für Peroxidverbindungen (Bleichmittel) und wasserlösliche organische Komplexbildner.

Im einzelnen gehören zu den Bleichmitteln Natriumperboratmono- oder tetrahydrat, die Alkalisalze der Peroxomono- oder Peroxodischwefelsäure, die Alkalisalze der Peroxodiphosphorsäure ($H_4P_2O_8$). Als Stabilisator für diese Bleichmittel fungiert z.B. wasserlösliches, gefälltes Magnesiumsilikat. Organische Komplexbildner sind die Alkalisalze der Iminodiessigsäure, Nitrilotriessigsäure, Ethylendiamintetraessigsäure, Methylendiphosphonsäure, 1-Hydroxyethan-1,1-diphosphonsäure und Nitrilotrismethylenphosphonsäure.

Waschhilfsstoffe, die das Schmutztragevermögen von Waschflotten erhöhen, wie Carboxymethylcellulose, Carboxymethylstärke, Methylcellulose oder Copolymere von Maleinsäureanhydrid mit Methylvinylether, Schaumregulatoren, wie Mono- und Dialkylphosphorsäureester mit 16 bis 20 C-Atomen im Alkylrest sowie optische Aufheller, Desinfizienzien und/oder proteolytische Enzyme können ebenfalls zusätzliche Bestandteile des weichmachenden Waschmittels sein.

Beispiel 1 - (Herstellung von Acrylsäure-1-Phenylvinyl-1-phosphonsäure-Copolymer analog dem Stand der Technik)

In einem 2-Liter-Mehrhalskolben mit Rührer, Rückflußkühler, Thermometer und Tropftrichter werden 216 g (3 mol) Acryl-

säure und 110,4 g (0,6 mol) 1-Phenylvinyl-1-phosphonsäure in 326 ml Wasser unter Inertgasatmosphäre zum Sieden erhitzt. Innerhalb von 18 h werden 15 g Kaliumperoxidisulfat als 5 %ige wäßrige Lösung zugetropft.

Als Produkt erhält man 952 g einer wäßrigen, viskosen Lösung, die laut ^{31}P-NMR-Spektroskopie frei von monomerer 1-Phenylvinyl-1-phosphonsäure ist.

Beispiel 2 - (Herstellung von Acrylsäure-Propen-2-phosphonsäure-Copolymer analog dem Stand der Technik)

In einer Apparatur analog Beispiel 1 werden 240 g (3,3 mol) Acrylsäure und 40,3 g (0,33 mol) Propen-2-phosphonsäure in 500 ml Wasser zum Sieden erhitzt. Durch Zugabe von 5 ml 5%iger Kaliumperoxidisulfat-Lösung als Radikalstarter wird die Polymerisation in Gang gesetzt. Nach 15 min. erhält man 780 g einer viskosen, farblosen Lösung, deren Restmonomeren-Gehalt an Propen-2-phosphonsäure ^{31}P-NMR-spektroskopisch bestimmt wird. 90 % der eingesetzten Phosphonsäure liegen polymergebunden vor.

Beispiel 3 - Labortest Calciumbindevermögen

Ermittelt wurde die Menge Komplexbildner in Form des bei pH 10 vorliegenden Natriumsalzes, die zum Wiederauflösen einer gegebenen Menge an frisch gefälltem $CaCO_3$-Niederschlag erforderlich ist. Diese Methode ist im Gegensatz zur z.B. Calciumsensitiven Elektrode auch bei erhöhter Temperatur einsetzbar. Bleibt die Lösung bei gleichen Mengenverhältnissen wie bei 20°C auch bei 60°C klar, so gilt der 20-°C-Wert auch für die erhöhte Temperatur. Die Methode ist mit einem Fehler in der Größenordnung von $\pm$ 5 % behaftet, da die Titrationsgeschwindigkeit das Titrationsergebnis beeinflußt. Die resultierenden

Zahlenwerte geben also nur einen Hinweis auf die Größenordnung des Calciumbindevermögens. Im allgemeinen nimmt das Calciumbindevermögen mit steigender Temperatur ab.
Die Ergebnisse sind in Tabelle I dargestellt.

Beispiel 4 - Labortest Dispergierverhalten

In einem Hartglasbecher wurden in 100 ml Wasser von 23°d, das mit Natronlauge auf pH 10 eingestellt war, 0,2 g des zu prüfenden Dispergiermittels vorgelegt und 0,5 Gew% Eisenoxid-Pigment (Bayferrox® 130) zugegeben. Es wurde 5 min. mit 2 000 UpM mit einem Sägezahnrührer von 40 mm Scheibendurchmesser dispergiert. Für die vorliegenden Versuche wurde gegebenenfalls der pH nochmal auf 10 nachgestellt. 30 ml der Dispersion wurden in einen PVC-Becher gegeben, ein Filterpapierstreifen (mittel- bis weitporig, 90 g/m^2) eingehängt und die Flüssigkeitssäule 2 h aufsteigen gelassen. Je nach Mitwandern des Pigments wurde die Benotung 1 (sehr gut), 2 (gut), 3 (mäßig), 4 (schlecht) vorgenommen. Die Ergebnisse sind Tabelle I zu entnehmen.

Beispiel 5 - "Threshold"-Test

Die Thresholdwirkung kann durch Streulichtmessung (TYNDALL-Effekt) sichtbar gemacht werden. Zur Messung eingesetzt werden $CaCO_3$-Trüben, die durch Vereinigen von
225 ml Wasser (56° d $CaCl_2$ Härte)
mit 25 ml $NaHCO_3$-Lösung (Molverhältnis $CaCl_2$: $NaHCO_3$ = 1:1,15)
in Gegenwart von 80 ppm Prüfsubstanz hergestellt werden. Bei Raumtemperatur wird dann mittels eines Streulichtphotometers der Trübungsverlauf verfolgt und beurteilt.

Die Beurteilung erfolgt nach folgender Notenskala

Note	4 (schlecht)	= Blindprobe
	3 (mäßig)	- deutliche Verringerung des Trübungsniveaus gegenüber Blindwert
	2 (gut)	- Auftreten der Trübung nach deutlicher Verzögerung bzw. stark reduzierte Trübung
	1 (sehr gut)	- keine Trübung innerhalb von 45 min.

Die Ergebnisse sind in Tabelle I wiedergegeben..

Beispiel 6 - Waschversuch

Verschiedene Testgewebe (Frottee, EMPA-Baumwolle (EMPA = Eidgenössiche Materialprüfungsanstalt St. Gallen, Schweiz), WFK-Baumwolle (WFK = Wäschereiforschung Krefeld), WFK-Polyester/Baumwolle, Doppelripp) wurden 20-mal bei 93°C und 18° d mit einem Versuchswaschmittel A folgender Zusammensetzung gewaschen (Dosierung je 150 g Vor- und Hauptwäsche):

A:	(Gew%)
NTPP	22,0
Alkylbenzolsulfonat	7,0
Nichtionische Tenside	4,0
Seife	3,5
Carboxymethylcellulose	1,5
Ethylendiamintetraacetat (EDTA)	0,2
Optischer Aufheller	0,2
Enzyme	0,25
$NaBO_3 \cdot 4\ H_2O$	20,0
Na-Disilikat	5,0
Mg-Silikat	2,0
Na_2SO_4	34,35

Anschließend wurde durch Veraschung bei 800°C die anorganische Gewebeinkrustierung ermittelt.

Durch Wiederholung des Versuches unter Zugabe von 1 Gew% Copolymer Acrylsäure/1-Phenylvinyl-1-phosphonsäure (ACS/PVP; Molverhältnis 10 : 1), bezogen auf die Waschmittelmenge, konnte die anorganische Gewebeinkrustierung deutlich gesenkt werden (Tabelle II).

Beispiel 7 - Waschversuch

EMPA-Baumwolle wie in Beispiel 6 wurde 25-mal bei 60°C und 18° d mit einem Versuchswaschmittel B der folgenden Zusammensetzung gewaschen (Dosierung 160 g, nur Klarwäsche):

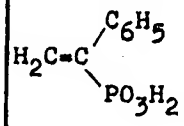
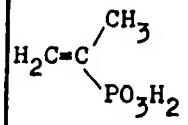
B:	(Gew%)
NTPP	25
Zeolith A	15
Soda	1,7
Natriumperborat-Tetrahydrat	22
Anionische Tenside	8,4
Nichtionische Tenside	3,6
Seifen	3,8

Die anorganische Gewebeinkrustierung wurde durch Veraschen bei 800°C ermittelt. Der Versuch wurde wiederholt in Gegenwart von 1,6 Gew% Copolymer gemäß Beispiel 2, bezogen auf die Waschmittelmenge, wodurch fast die gleiche Senkung der Gewebeinkrustierung erreicht wurde wie durch Zusatz von 3,1 Gew% Natriumnitrilotriacetat (NTA) (Tabelle II).

Beispiel 8 - Waschversuch

Ein noch besseres Ergebnis wurde bei Versuchswaschmittel B erreicht durch Zusatz von 1,6 Gew% Copolymer Acrylsäure-1-Phenylvinyl-1-phosphonsäure (ACS/PVP; Molverhältnis 10 : 1) (Tabelle II).

TABELLE I

Monomer a	Monomer b	Mol-verhältnis a : b	Beispiel 3 Ca-Bindevermögen (mg Ca/g Na-Salz) 20°C	Beispiel 3 Ca-Bindevermögen (mg Ca/g Na-Salz) 60°C	Beispiel 4 Dispergier-test Note	Beispiel 5 Threshold-test Note
CH_2=CHCOOH		10 : 1	250	250	1	1
		5 : 1 Beispiel 1	294	294	1	1
CH_2=CHCOOH		10 : 1 Beispiel 2	184	146	1	2
		3 : 1	202	202	1	1
zum Vergleich: $Na_5P_3O_{10}$ (NTPP)			130	130	2	1
	$Na(CH_2COONa)_3$		194	170	3-4	4
	Zeolith A		114 a)			

a) Herstellerangabe, Rücktitration mit EDTA nach Filtration

T A B E L L E II

Gew% Asche nach 20 Waschzyklen

Produkt	Frottee	EMPA-Baumwolle	WFK-Baumwolle	WFK-Polyester/Baumwolle	Doppelripp
A	3.18	2.68	1.78	1.10	2.98
A + 1 Gew% ACS/PVP	1.57	2.30	1.40	0.33	1.43

Gew% Asche nach 25 Waschzyklen

Produkt	EMPA-Baumwolle
B	8.3
B + 3,1 Gew% NTA	5.9
B + 1,6 Gew% ACS/PVP (10 : 1)	5.9
B + 1,6 Gew% ACS/Propenphosphonsäure (10 : 1)	6.1

HOECHST AKTIENGESELLSCHAFT

Wasch- und Reinigungsmittel

Patentansprüche:

1. Wasch- und Reinigungsmittel mit 5 bis 70 Gew% mindestens eines Tensids, 0,1 bis 50 Gew% mindestens eines Gerüststoffes sowie üblichen Waschhilfsstoffen, gekennzeichnet durch folgende Gerüststoffgehalte:

   a) 0,1 bis 25 Gew% eines Copolymers, erhältlich durch an sich bekannte Copolymerisation folgender Monomere:

      aa) 40 bis 99,9 Mol % ethylenisch ungesättigter Carbonsäuren oder deren Alkalisalze der allgemeinen Formel $R^1(R^2)C=C(R^3)COOX$,
      worin X = H, Alkalimetall;
      R^2 = H, COOX, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl oder substituiertes Phenyl;
      R^1, R^3 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl bedeuten,

      oder deren Anhydride;

      bb) 0,1 bis 40 Mol% ethylenisch ungesättigter Phosphonsäuren oder deren Alkalisalze der allgemeinen Formel $R^4(R^5)C=C(R^6)PO_3X_2$,
      worin X = H, Alkalimetall;
      R^4, R^5 = H, C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;
      R^6 = C_1-C_4-Alkyl, C_5-C_8-Cycloalkyl, Phenyl, substituiertes Phenyl;

Translation of European Patent Application 0 161 596 A2

Filed May 4, 1985 with priority of May 18, 1984, DE 34 18 494

Inventors: Grosse et al
Assigned to Hoechst AG, Frankfurt

(54) Washing and Cleaning Agent

(57) The washing and cleaning agent of the invention, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, is characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

Ex 6-8

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

The invention also pertains to the use of the copolymer as a builder or builder additive in washing and cleaning agents.

WASHING AND CLEANING AGENT

One detergent ingredient that is decisive for successful washing with washing and cleaning agents is pentasodium triphosphate, $Na_5P_3O_{10}$, also known industrially as sodium tripolyphosphate or NTPP. The compound has the following effective properties:

- complexing of alkaline earth ions,
- selective adsorption at boundary faces of the textile substrate and dirt,
- reinforcing the action of anion surfactants,
- dispersion of pigment soil,
- alkaline reaction,
- buffer action,
- "threshold" action,
- builder for washing and cleaning agents.

Of particular significance in the cleaning power of modern detergents are the calcium binding capacity, the dispersion action, and the "threshold" effect, which is understood to mean the property of a substance, used in a substoichiometric ratio, of delaying or hindering the settling out of hardness salts.

One undesired side effect of NTPP is that - along with phosphates from other sources, such as fertilizers, feces, soil erosion, and may others - it contributes to introducing phosphorus into bodies of water. Excess phosphorus concentrations, especially in stagnant and slow-flowing bodies of water, can lead to eutrophication.

For this reason, comparably well suited substitutes for phosphates have long been sought. In various countries, official steps have been taken to limit or entirely forbid

the use of NTPP in detergents.

In the Federal Republic of Germany, lowering the phosphate content in detergents meant poorer results from washing. In particular, increased inorganic fabric incrustation was observed; there is no doubt that excessive fabric incrustation makes the washed product less useful.

It was accordingly the object to find phosphate substitutes that improve the action of the builder system and thus the action of the detergent again.

Many substances have been discussed as a complete or partial substitute for NTPP, examples being zeolite A, trisodium nitrilotriacetate and sodium citrate. For various reasons - in part, ecological concerns, lack of economy, performance that is not satisfactory in every respect - until now no substance has been found that by itself could be successful as an NTPP substitute. On the contrary, the opinion was increasingly expressed that combinations of builders or builder additives could lead to optimal performance. Compounds that in relatively low usage concentrations exert pronounced influence on the builder system are known as builder additives.

The invention relates to a washing and cleaning agent, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, which is characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

The invention also pertains to the use as a builder or builder additive, in washing and cleaning agents, of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

a) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

b) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general

formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

c) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

Preferably, 65 to 98 Mol % of ethylenically unsaturated carboxylic acids, 2 to 30 Mol % of ethylenically unsaturated phosphonic acids and 0 to 5 Mol % of other olefinically unsaturated compounds are polymerized to form the copolymers used according to the invention. These copolymers of the invention are incorporated as builders or builder additives, preferably together with pentasodium triphosphate, zeolite A or trisodium nitrilotriacetate, as further builders into the washing and cleaning agents.

To prepare the copolymers, preferably acrylic acid, methacrylic acid, vinyl acetic acid or maleic acid anhydride are used as ethylenically unsaturated carboxylic acids or their anhydrides, and preferably 1-phenylvinyl-1-phosphonic acid or propene-2-phosphonic acid is used as ethylenically unsaturated phosphonic acids. The colymerization of other olefinically unsaturated compounds without carboxylic or phosphonic acid groups is unnecessary, although for instance ethylene, butadiene, chloroprene, acrylamide, methacrylamide, acrylamidosulfonic acid, vinylsulfonic acid, allylsulfonic acid, vinyl acetate, hydroxyethyl acrylate or hydroxypropyl acrylate, vinyl glycol, or methyl (meth)acrylate may also be incorporated by polymerization.

The copolymers functioning according to the invention as builders at the same time have the character of polymeric

carboxylic acids and phosphonic acids, and they develop their excellent incrustation-inhibiting and dispersing properties equally with various builder systems, such as in combination with NTPP and zeolite A.

The monomeric ethylenically unsaturated carboxylic acids are in general products available on a large industrial scale; the monomeric ethylenically unsaturated phosphonic acids are easily and economically obtainable, for instance by reacting ketones with phosphorus trichloride (German Published Patent Application DE-OS 33 23 392) or with tetraphosphorus hexoxide (German Published Patent Applications DE-OS 31 25 329 and DE-OS 32 10 419).

DE-OS 18 01 411 describes the use of water-soluble salts of organic polymer compounds that contain phosphonic and carboxylic acid groups in the side chains as general builders in washing and cleaning agents. Vinyl phosphonic acid serves as the phosphonic acid monomer here. Using this builder alone, however, is not commercially feasible.

The production of the copolymers, functioning according to the invention as builders, from the aforementioned monomers by radical polymerization is known per se or can be performed by comparable recipes (see for instance DE-OS 24 55 624, Example 10, and DE-OS 18 01 411, page 5).

The builders contained according to the invention in the washing and cleaning agents may be incorporated into the washing and cleaning agents in the usual way by spray drying, mixing, or a spray mist mixing process. Another advantage of the builders or builder additives according to the invention is their contribution to "anti-caking", that is, to prevent demixing phenomena in detergent slurries that are rich in nonionic surfactants.

The washing and cleaning agents according to the

invention are distinguished by excellent outcomes of washing. They have a markedly high calcium binding capacity as well as excellent dispersing and threshold action, so that long with their incrustation-inhibiting action, pronounced graying-inhibiting properties must be ascribed to them.

The washing and cleaning agent of the invention contains as surfactants preferably those of an anionic, amphionic (ampholytic) or nonionic nature.

Anionic surfactants are understood to mean the water-soluble salts of higher fatty acids or colophonic acids such as soda or potash soaps from coconut, palm kernel or rapeseed oil as well as from tallow, and mixtures thereof. Also included in this term are higher alkyl-substituted aromatic sulfonates, such as alkyl benzene sulfonates with from 9 to 14 carbon atoms in the alkyl radical, alkyl naphthalene sulfonates, alkyl toluene sulfonates, alkyl xylene sulfonates, or alkyl phenol sulfonates; fatty alcohol sulfonates ($R-CH_2-O-SO_3Na$; $R = C_{11-17}$) or fatty alcohol ether sulfates, such as alkali lauryl sulfate or alkali hexadecyl sulfate, triethanolamine lauryl sulfate, sodium or potassium oleyl sulfate, sodium or potassium salts of lauryl sulfate ethoxylated with from 2 to 6 Mols of ethylene oxides. Other suitable anionic surfactants are secondary linear alkane sulfonates as well as α-olefin sulfonates with a chain length of 12 to 20 carbon atoms.

Nonionic surfactants are understood to be those compounds that have an organic hydrophobic group as well as a hydrophilic radical, such as the condensation products of alkyl phenols or higher fatty alcohols with ethylene oxide, the condensation products of polypropylene glycol with ethylene oxide or propylene oxide, the condensation products of ethylene oxide with the reaction product of ethylene

diamine and propylene oxide, as well as long-chain tertiary amine oxides ($C_{12}H_{25} - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} \rightarrow O$).

Finally, surfactants with amphionic (ampholytic) character are the following compounds:

Derivatives of aliphatic, secondary and tertiary amines or quaternary ammonium compounds with from 8 to 18 carbon atoms and a hydrophilic group in the aliphatic radical, such as sodium-3-dodecylaminopropionate, sodium-3-dodecylaminopropane sulfonate, 3-(N,N-dimethyl-N-hexadecylamino)-1-propane sulfonate or fatty acid aminoalkyl-N,N-dimethyl acetobetaine in which the fatty acid contains from 8 to 18 carbon atoms and the alkyl radical contains from 1 to 3 carbon atoms.

Suitable builder substances for the detergents of the invention are inorganic or organic salts that react slightly acidically, neutrally or in alkaline fashion, in particular inorganic or organic complexing agents.

Usable salts that react slightly acidically, neutrally or in alkaline fashion are for instance the bicarbonates, carbonates or silicates of alkalis, and also mono-, di- or trialkali orthophosphates. Di- or tetraalkali pyrophosphates, as complexing agents, known metaphosphates, alkali sulfates and the alkali salts of organic, not capillary-active sulfonic acids containing from 1 to 8 carbon atoms, carboxylic acids and sulfocarboxylic acids. These include for instance water-soluble salts of benzene sulfonic acid, toluene sulfonic acid or xylene sulfonic acid, water-soluble salts of sulfoacetic acid, sulfobenzoic acid, or salts of sulfodicarboxylic acids as well as the salts of

acetic acid, lactic acid, citric acid, tartaric acid, oxydiacetic acid ($HOOC-CH_2-O-CH_2-COOH$), oxydisuccinic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, polyacrylic acid and polymaleic acid.

As complex-forming builders, the weakly acidically reacting metaphosphates and the alkaline-reacting polyphosphates are also suitable, in particular tripolyphosphate. They may be substituted entirely or in part by organic complexing agents. The organic complexing agents include for instance nitrilotriacetic acid, ethylenediaminetriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, polyalkylene polyamine-N-polycarboxylic acids and other known organic complexing agents, and a combination of different complexing agents can also be employed.

Detergent adjuvants according to the invention include such products as the alkali or ammonium salts of sulfuric acid, silicic acid, carbonic acid, boric acid, alkylene phosphonic acid, hydroxyalkylene phosphonic acid or aminoalkylene phosphonic acid, as well as bleaching agents, stabilizers for peroxide compounds (bleaching agents), and water-soluble organic complexing agents.

Specifically, the bleaching agents include sodium perborate mono- or tetrahydrate, the alkali salts of peroxomono- or peroxodisulfuric acid, and the alkali salts of peroxodiphosphoric acid ($H_4P_2O_8$). As stabilizers for these bleaching agents, water-soluble, precipitated magnesium silicate is for instance used. Organic complexing agents are the alkali salts of iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, methylene diphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, and nitrilotris-methylene phosphonic acid.

Detergent adjuvants that increase the dirt-carrying capacity of solutions of detergent and water, such as carboxymethylcellulose, carboxymethyl starch, methylcellulose, or copolymers of maleic acid anhydride with methylvinyl ether, foam regulators, such as mono- and dialkylphosphoric acid esters with 16 to 20 carbon atoms in the alkyl radical, and optical brighteners, disinfectants, and/or proteolytic enzymes may also be additional components of the softening detergent.

Example 1 (Preparation of acrylic acid-1-phenylvinyl-1-phosphonic acid copolymer analogous to the prior art)

In a two-liter multinecked flask with an agitator, reflux cooler, thermometer and droplet funnel, 216 g (3 Mols) of acrylic acid and 110.4 g (0.6 Mols) of 1-phenylvinyl-1-phosphonic acid are heated in 326 ml of water under an inert gas atmosphere until boiling. Over 18 hours, 15 g of potassium peroxide disulfate is added drop by drop in the form of a 5% aqueous solution.

As the product, 952 g of an aqueous viscous solution are obtained, the solution being free of monomeric 1-phenylvinyl-1-phosphonic acid, according to ^{31}P-NMR spectroscopy.

Example 2 (Preparation of acrylic acid propene-2-phosphonic acid copolymer analogous to the prior art)

In an apparatus analogous to Example 1, 240 g (3.3 Mols) of acrylic acid and 40.3 g (0.33 Mols) of propene-2-phosphonic acid are heated until boiling in 500 ml of water. By adding 5 ml of 5% potassium peroxide disulfate solution as

a radical starter, the polymerization is put in motion. After 15 minutes, 780 g of a viscous colorless solution are obtained, in which the residual monomer content of propene-2-phosphonic acid is determined by ^{31}P-NMR spectroscopy. 90% of the phosphonic acid used is in polymer-bound form.

Example 3: Laboratory test of calcium binding capacity

This test determined the quantity of complexing agent, in the form of the sodium salt at a pH of 10, that is needed to re-dissolve a given quantity of freshly precipitated $CaCO_3$ precipitate. This method, in contrast to the calcium-sensitive electrode, for instance, can also be used at elevated temperature. If for the same quantity ratios the solution remains as clear at 60° as at 20°C, then the 20°C value applies to the elevated temperature as well. The method involves an error on the order to magnitude of ± 5%, because the titration speed affects the outcome of titration. The resultant numerical values accordingly are merely an indication of the order of magnitude of the calcium binding capacity. In general, the calcium binding capacity decreases as the temperature increases. The results are shown in Table I.

Example 4: Laboratory test of dispersing performance

In a hard glass beaker, in 100 ml of water at 23° d, which was adjusted to a pH of 10 with soda lye, 0.2 g of the dispersing agent to be tested were placed, and 0.5 weight % of iron oxide pigment (Bayferrox(R) 130) were added. Dispersion was performed for 5 minutes at 2000 rpm with a sawtooth agitator with a disk diameter of 40 mm. For the

present tests, the pH was readjusted to 10 again. 30 ml of the dispersion were placed in a PVC beaker and a filter paper strip (medium- to wide-pore, 90 g/m^2) was suspended in it, and the liquid column was allowed to rise to two hours. Depending on the co-migration of the pigment, the grades assigned were 1 (very good), 2 (good), 3 (mediocre), 4 (poor). The results can be found in Table I.

Example 5: Threshold test

The threshold action can be made visible by scattered light measurement (the Tyndall effect). $CaCO_3$ slurries were used for the measurement, which were prepared by combining

225 ml of water 56° d ($CaCl_2$ hardness)

with 25 ml $NaHCO_3$ solution (Molar ratio $CaCl_2$:$NaHCO_3$ = 1:1.15)

in the presence of 80 ppm of test substance. At room temperature, by means of a scattered-light photometer, the course of turbidity was then followed and assessed.

The assessment was done by the following grading scale:

grade 4 (poor) = blind specimen

3 (mediocre) = marked lessening in the level of turbidity compared with the blind value

2 (good) = occurrence of turbidity after a pronounced delay, or severely reduced turbidity

1 (very good) = no turbidity within 45 minutes

The results are shown in Table I.

Example 6: Wash test

Various test fabrics (terry cloth, EMPA cotton [EMPA = Eidgenössische Materialprüfungsanstalt, St. Gallen, Switzerland], WFK cotton [WFK = Wäschereiforschung Krefeld, Germany], WFK polyester-cotton, 2/2 rib) were washed 20 times at 93°C and 18° d with a test detergent A of the following composition (dosage per 150 g in pre-wash and main wash).

A:	weight %
NTPP	22.0
Alkyl benzene sulfonate	7.0
Nonionic surfactants	4.0
Soap	3.5
Carboxymethylcellulose	1.5
Ethylenediaminetetraacetate (EDTA)	0.2
Optical brightener	0.2
Enzymes	0.25
$NaBO_3 \cdot 4H_2O$	20.0
Sodium disilicate	5.0
Magnesium silicate	2.0
Na_2SO_4	34.35

Next, the inorganic fabric incrustation was ascertained by incineration at 900°C:

By repeating the test with the addition of 1 weight % of copolymer acrylic acid/1-phenylvinyl-1-phosphonic acid (ACS/PVP: molar ratio 10:1), referred to the quantity of detergent, it was possible to lower the inorganic fabric incrustation markedly (Table II).

Example 7: Wash test

EMPA cotton as in Example 6 was washed 25 times at 60°C and 18° d with a test detergent B of the following composition (dosage 160 g, main wash only:

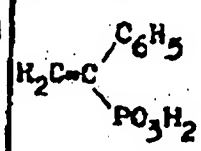
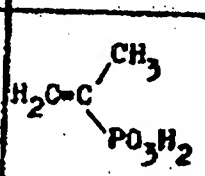
B:	weight %
NTPP	25.0
Zeolite A	15.0
Soda	1.7
Sodium perborate tetrahydrate	22.0
Anionic surfactants	8.4
Nonionic surfactants	3.6
Soaps	3.8

The inorganic fabric incrustation was ascertained by incineration at 800°C. The test was repeated in the presence of 1.6 weight % of copolymer in accordance with Example 2, referred to the quantity of detergent, by which virtually the same reduction in fabric incrustation was attained as by the addition of 3.1 weight % of sodium nitrilotriacetate (NTA) (Table II).

Example 8: Wash test

An even better result was attained with test detergent B by adding 1.6 weight % of copolymer acrylic acid-1-phenylvinyl-1-phosphonic acid (ACS/PVP; molar ratio 10:1) (Table II).

Table I

Monomer [a]	Monomer [b]	Molar ratio a : b	Example 3 Calcium binding capacity (mg Ca/g Na-salt) 20°C	60°C	Example 4 Dispersion test Grade	Example 5 Threshold test Grade
CH_2=CHCOOH		10 : 1	250	250	1	1
		5 : 1 Example 1	294	294	1	1
CH_2=CHCOOH		10 : 1 Example 2	184	146	1	2
		3 : 1	202	202	1	1
For comparison: $Na_5P_3O_{10}$ (NTPP)			130	130	2	1
$Na(CH_2COONa)_3$			194	170	3-4	4
Zeolite A			114 a)			

a) Manufacturer indication, back titration with EDTA after filtration

Table II

Weight % of ash after 20 washing cycles

Product	Terry cloth	EMPA cotton	WFK cotton	WFK polyester-cotton	2/2 Rib
A	3.18	2.68	1.78	1.10	2.98
A + 1 Weight % ACS/PVP	1.57	2.30	1.40	0.33	1.43

Weight % of ash after 25 washing cycles

Product	EMPA cotton
B	8.3
B + 3,1 Weight % NTA	5.9
B + 1,6 Weight % ACS/PVP (10:1)	5.9
B + 1,6 Weight % ACS/ propenephosphonic acid (10:1)	6.1

Claims:

1. A washing and cleaning agent, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

2. The use as a builder or builder additive, in washing and cleaning agents, of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

a) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

b) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

c) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

J A N M c L I N C L A Y B E R G
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Total number of pages in this transmission: 21

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Notes on the translation:

I summarized the cover page information; "(54)" is of course the title and "(57)" the abstract. Let me know if you need the whole thing (names and addresses in detail!).

The subject is Wasch- und Reinigungsmittel, or "washing and cleaning agent" - a single agent. But Waschmittel by itself means "detergent" and I used that for that term on its own. The title could thus be "detergent and cleaning agent", but I did not translate it that way in case that would sound like two agents instead.

Pigmentschmutz: - My Dictionary of Washing says "pigment soil" or "particulate soil" - I picked the first one as closest to the German.

"Threshold" action is in quotes because the English word is used in the German case; strictly speaking it might then not have to be in quotes in English.

Various "DE-OS" references are cited - such as "German Published Patent Applications DE-OS 31 25 329 and DE-OS 32 10 419" - DE-OS means the published, non-examined version of the German application but I thought saying so twice was enough.

Slight formal things: The abstract, spec and claim 1 all have a period at the end of paragraph cc), but the claim and presumably the other passages actually continue for one more paragraph. Left as is.

"Using this builder alone, however, is not commercially feasible or cannot be performed economically and hence is not worthwhile commercially (German wirtschaftlich - commercial, economical).

"graying-inhibiting properties" - or soil anti-redeposition properties - preventing washed-out dirt from being absorbed back into the clothes and graying them. You know this of course - I wanted to note the other option though.

Translation page 9, "sodium or potassium oleyl sulfate, sodium or potassium salts" - in each case, "sodium" is not an element but modifies the part after "potassium".

Translation page 9, "Usable salts that react slightly acidically, neutrally or in alkaline fashion are for instance the bicarbonates, carbonates or silicates of alkalis, and also mono-, di- or trialkali orthophosphates. Di- or tetraalkali pyrophosphates, as complexing agents, known metaphosphates, alkali sulfates and the alkali salts of organic, not capillary-active sulfonic acids containing from 1 to 8 carbon atoms, carboxylic acids and sulfocarboxylic acids." Sic - the second "sentence" is a fragment (no verb). Maybe it should have been punctuated differently: "...and also mono-, di- or trialkali orthophosphates, di- or tetraalkali pyrophosphates, and as complexing agents, known metaphosphates,..." - would that make sense chemically?

US page 10, "carbonic acid" - the IUPAC-preferred term is dihydrogentrioxocarbonate. Noted for the record. To me, simpler is better for now.

US page 10, before Example 1, "optical brighteners, disinfectants, and/or proteolytic enzymes may also be additional components of the softening detergent." - weichmachendes Waschmittel. I guess the detergent with these additives also softens clothes? The usual word for fabric softener (added to the rinse cycle) is Weichspüler.

Example 4, "a hard glass beaker" - also known as a resistance-glass beaker, if that is a better term.

In the examples, °C are mentioned, but also ° d; at first I thought the latter was a typo for C but it seems to be a measure of hardness. Shore hardness is usually D? Apparently this "d" is a measure of water hardness; for example: "100 ml of water at 23° d".

US page 15, "acrylic acid/1-phenylvinyl-1-phosphonic acid" - the slash is probably a typo for a hyphen but left as is; German page 12, line 5.

Translation of European Patent Application 0 161 596 A2

Filed May 4, 1985 with priority of May 18, 1984, DE 34 18 494

Inventors: Grosse et al

Assigned to Hoechst AG, Frankfurt

(54) Washing and Cleaning Agent

(57) The washing and cleaning agent of the invention, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, is characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

The invention also pertains to the use of the copolymer as a builder or builder additive in washing and cleaning agents.

WASHING AND CLEANING AGENT

One detergent ingredient that is decisive for successful washing with washing and cleaning agents is pentasodium triphosphate, $Na_5P_3O_{10}$, also known industrially as sodium tripolyphosphate or NTPP. The compound has the following effective properties:

- complexing of alkaline earth ions,
- selective adsorption at boundary faces of the textile substrate and dirt,
- reinforcing the action of anion surfactants,
- dispersion of pigment soil,
- alkaline reaction,
- buffer action,
- "threshold" action,
- builder for washing and cleaning agents.

Of particular significance in the cleaning power of modern detergents are the calcium binding capacity, the dispersion action, and the "threshold" effect, which is understood to mean the property of a substance, used in a substoichiometric ratio, of delaying or hindering the settling out of hardness salts.

One undesired side effect of NTPP is that - along with phosphates from other sources, such as fertilizers, feces, soil erosion, and may others - it contributes to introducing phosphorus into bodies of water. Excess phosphorus concentrations, especially in stagnant and slow-flowing bodies of water, can lead to eutrophication.

For this reason, comparably well suited substitutes for phosphates have long been sought. In various countries, official steps have been taken to limit or entirely forbid

the use of NTPP in detergents.

In the Federal Republic of Germany, lowering the phosphate content in detergents meant poorer results from washing. In particular, increased inorganic fabric incrustation was observed; there is no doubt that excessive fabric incrustation makes the washed product less useful.

It was accordingly the object to find phosphate substitutes that improve the action of the builder system and thus the action of the detergent again.

Many substances have been discussed as a complete or partial substitute for NTPP, examples being zeolite A, trisodium nitrilotriacetate and sodium citrate. For various reasons - in part, ecological concerns, lack of economy, performance that is not satisfactory in every respect - until now no substance has been found that by itself could be successful as an NTPP substitute. On the contrary, the opinion was increasingly expressed that combinations of builders or builder additives could lead to optimal performance. Compounds that in relatively low usage concentrations exert pronounced influence on the builder system are known as builder additives.

The invention relates to a washing and cleaning agent, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, which is characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

The invention also pertains to the use as a builder or builder additive, in washing and cleaning agents, of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

a) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

b) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general

formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

c) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

Preferably, 65 to 98 Mol % of ethylenically unsaturated carboxylic acids, 2 to 30 Mol % of ethylenically unsaturated phosphonic acids and 0 to 5 Mol % of other olefinically unsaturated compounds are polymerized to form the copolymers used according to the invention. These copolymers of the invention are incorporated as builders or builder additives, preferably together with pentasodium triphosphate, zeolite A or trisodium nitrilotriacetate, as further builders into the washing and cleaning agents.

To prepare the copolymers, preferably acrylic acid, methacrylic acid, vinyl acetic acid or maleic acid anhydride are used as ethylenically unsaturated carboxylic acids or their anhydrides, and preferably 1-phenylvinyl-1-phosphonic acid or propene-2-phosphonic acid is used as ethylenically unsaturated phosphonic acids. The colymerization of other olefinically unsaturated compounds without carboxylic or phosphonic acid groups is unnecessary, although for instance ethylene, butadiene, chloroprene, acrylamide, methacrylamide, acrylamidosulfonic acid, vinylsulfonic acid, allylsulfonic acid, vinyl acetate, hydroxyethyl acrylate or hydroxypropyl acrylate, vinyl glycol, or methyl (meth)acrylate may also be incorporated by polymerization.

The copolymers functioning according to the invention as builders at the same time have the character of polymeric

carboxylic acids and phosphonic acids, and they develop their excellent incrustation-inhibiting and dispersing properties equally with various builder systems, such as in combination with NTPP and zeolite A.

The monomeric ethylenically unsaturated carboxylic acids are in general products available on a large industrial scale; the monomeric ethylenically unsaturated phosphonic acids are easily and economically obtainable, for instance by reacting ketones with phosphorus trichloride (German Published Patent Application DE-OS 33 23 392) or with tetraphosphorus hexoxide (German Published Patent Applications DE-OS 31 25 329 and DE-OS 32 10 419).

DE-OS 18 01 411 describes the use of water-soluble salts of organic polymer compounds that contain phosphonic and carboxylic acid groups in the side chains as general builders in washing and cleaning agents. Vinyl phosphonic acid serves as the phosphonic acid monomer here. Using this builder alone, however, is not commercially feasible.

The production of the copolymers, functioning according to the invention as builders, from the aforementioned monomers by radical polymerization is known per se or can be performed by comparable recipes (see for instance DE-OS 24 55 624, Example 10, and DE-OS 18 01 411, page 5).

The builders contained according to the invention in the washing and cleaning agents may be incorporated into the washing and cleaning agents in the usual way by spray drying, mixing, or a spray mist mixing process. Another advantage of the builders or builder additives according to the invention is their contribution to "anti-caking", that is, to prevent demixing phenomena in detergent slurries that are rich in nonionic surfactants.

The washing and cleaning agents according to the

invention are distinguished by excellent outcomes of washing. They have a markedly high calcium binding capacity as well as excellent dispersing and threshold action, so that long with their incrustation-inhibiting action, pronounced graying-inhibiting properties must be ascribed to them.

The washing and cleaning agent of the invention contains as surfactants preferably those of an anionic, amphionic (ampholytic) or nonionic nature.

Anionic surfactants are understood to mean the water-soluble salts of higher fatty acids or colophonic acids such as soda or potash soaps from coconut, palm kernel or rapeseed oil as well as from tallow, and mixtures thereof. Also included in this term are higher alkyl-substituted aromatic sulfonates, such as alkyl benzene sulfonates with from 9 to 14 carbon atoms in the alkyl radical, alkyl naphthalene sulfonates, alkyl toluene sulfonates, alkyl xylene sulfonates, or alkyl phenol sulfonates; fatty alcohol sulfonates ($R-CH_2-O-SO_3Na$; $R = C_{11-17}$) or fatty alcohol ether sulfates, such as alkali lauryl sulfate or alkali hexadecyl sulfate, triethanolamine lauryl sulfate, sodium or potassium oleyl sulfate, sodium or potassium salts of lauryl sulfate ethoxylated with from 2 to 6 Mols of ethylene oxides. Other suitable anionic surfactants are secondary linear alkane sulfonates as well as α-olefin sulfonates with a chain length of 12 to 20 carbon atoms.

Nonionic surfactants are understood to be those compounds that have an organic hydrophobic group as well as a hydrophilic radical, such as the condensation products of alkyl phenols or higher fatty alcohols with ethylene oxide, the condensation products of polypropylene glycol with ethylene oxide or propylene oxide, the condensation products of ethylene oxide with the reaction product of ethylene

diamine and propylene oxide, as well as long-chain tertiary amine oxides ($C_{12}H_{25} - \overset{CH_3}{\underset{CH_3}{N}} = O$).

Finally, surfactants with amphionic (ampholytic) character are the following compounds:

Derivatives of aliphatic, secondary and tertiary amines or quaternary ammonium compounds with from 8 to 18 carbon atoms and a hydrophilic group in the aliphatic radical, such as sodium-3-dodecylaminopropionate, sodium-3-dodecylaminopropane sulfonate, 3-(N,N-dimethyl-N-hexadecylamino)-1-propane sulfonate or fatty acid aminoalkyl-N,N-dimethyl acetobetaine in which the fatty acid contains from 8 to 18 carbon atoms and the alkyl radical contains from 1 to 3 carbon atoms.

Suitable builder substances for the detergents of the invention are inorganic or organic salts that react slightly acidically, neutrally or in alkaline fashion, in particular inorganic or organic complexing agents.

Usable salts that react slightly acidically, neutrally or in alkaline fashion are for instance the bicarbonates, carbonates or silicates of alkalis, and also mono-, di- or trialkali orthophosphates. Di- or tetraalkali pyrophosphates, as complexing agents, known metaphosphates, alkali sulfates and the alkali salts of organic, not capillary-active sulfonic acids containing from 1 to 8 carbon atoms, carboxylic acids and sulfocarboxylic acids. These include for instance water-soluble salts of benzene sulfonic acid, toluene sulfonic acid or xylene sulfonic acid, water-soluble salts of sulfoacetic acid, sulfobenzoic acid, or salts of sulfodicarboxylic acids as well as the salts of

acetic acid, lactic acid, citric acid, tartaric acid, oxydiacetic acid ($HOOC-CH_2-O-CH_2-COOH$), oxydisuccinic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, polyacrylic acid and polymaleic acid.

As complex-forming builders, the weakly acidically reacting metaphosphates and the alkaline-reacting polyphosphates are also suitable, in particular tripolyphosphate. They may be substituted entirely or in part by organic complexing agents. The organic complexing agents include for instance nitrilotriacetic acid, ethylenediaminetriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, polyalkylene polyamine-N-polycarboxylic acids and other known organic complexing agents, and a combination of different complexing agents can also be employed.

Detergent adjuvants according to the invention include such products as the alkali or ammonium salts of sulfuric acid, silicic acid, carbonic acid, boric acid, alkylene phosphonic acid, hydroxyalkylene phosphonic acid or aminoalkylene phosphonic acid, as well as bleaching agents, stabilizers for peroxide compounds (bleaching agents), and water-soluble organic complexing agents.

Specifically, the bleaching agents include sodium perborate mono- or tetrahydrate, the alkali salts of peroxomono- or peroxodisulfuric acid, and the alkali salts of peroxodiphosphoric acid ($H_4P_2O_8$). As stabilizers for these bleaching agents, water-soluble, precipitated magnesium silicate is for instance used. Organic complexing agents are the alkali salts of iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, methylene diphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, and nitrilotris-methylene phosphonic acid.

Detergent adjuvants that increase the dirt-carrying capacity of solutions of detergent and water, such as carboxymethylcellulose, carboxymethyl starch, methylcellulose, or copolymers of maleic acid anhydride with methylvinyl ether, foam regulators, such as mono- and dialkylphosphoric acid esters with 16 to 20 carbon atoms in the alkyl radical, and optical brighteners, disinfectants, and/or proteolytic enzymes may also be additional components of the softening detergent.

Example 1 (Preparation of acrylic acid-1-phenylvinyl-1-phosphonic acid copolymer analogous to the prior art)

In a two-liter multinecked flask with an agitator, reflux cooler, thermometer and droplet funnel, 216 g (3 Mols) of acrylic acid and 110.4 g (0.6 Mols) of 1-phenylvinyl-1-phosphonic acid are heated in 326 ml of water under an inert gas atmosphere until boiling. Over 18 hours, 15 g of potassium peroxide disulfate is added drop by drop in the form of a 5% aqueous solution.

As the product, 952 g of an aqueous viscous solution are obtained, the solution being free of monomeric 1-phenylvinyl-1-phosphonic acid, according to ^{31} P-NMR spectroscopy.

Example 2 (Preparation of acrylic acid propene-2-phosphonic acid copolymer analogous to the prior art)

In an apparatus analogous to Example 1, 240 g (3.3 Mols) of acrylic acid and 40.3 g (0.33 Mols) of propene-2-phosphonic acid are heated until boiling in 500 ml of water. By adding 5 ml of 5% potassium peroxide disulfate solution as

a radical starter, the polymerization is put in motion. After 15 minutes, 780 g of a viscous colorless solution are obtained, in which the residual monomer content of propene-2-phosphonic acid is determined by ^{31} P-NMR spectroscopy. 90% of the phosphonic acid used is in polymer-bound form.

Example 3: Laboratory test of calcium binding capacity

This test determined the quantity of complexing agent, in the form of the sodium salt at a pH of 10, that is needed to re-dissolve a given quantity of freshly precipitated $CaCO_3$ precipitate. This method, in contrast to the calcium-sensitive electrode, for instance, can also be used at elevated temperature. If for the same quantity ratios the solution remains as clear at 60° as at 20°C, then the 20°C value applies to the elevated temperature as well. The method involves an error on the order to magnitude of ± 5%, because the titration speed affects the outcome of titration. The resultant numerical values accordingly are merely an indication of the order of magnitude of the calcium binding capacity. In general, the calcium binding capacity decreases as the temperature increases. The results are shown in Table I.

Example 4: Laboratory test of dispersing performance

In a hard glass beaker, in 100 ml of water at 23° d, which was adjusted to a pH of 10 with soda lye, 0.2 g of the dispersing agent to be tested were placed, and 0.5 weight % of iron oxide pigment (Bayferrox$^{(R)}$ 130) were added. Dispersion was performed for 5 minutes at 2000 rpm with a sawtooth agitator with a disk diameter of 40 mm. For the

present tests, the pH was readjusted to 10 again. 30 ml of the dispersion were placed in a PVC beaker and a filter paper strip (medium- to wide-pore, 90 g/m²) was suspended in it, and the liquid column was allowed to rise to two hours. Depending on the co-migration of the pigment, the grades assigned were 1 (very good), 2 (good), 3 (mediocre), 4 (poor). The results can be found in Table I.

Example 5: Threshold test

The threshold action can be made visible by scattered light measurement (the Tyndall effect). $CaCO_3$ slurries were used for the measurement, which were prepared by combining

225 ml of water 56° d ($CaCl_2$ hardness)

with 25 ml $NaHCO_3$ solution (Molar ratio $CaCl_2$:$NaHCO_3$ = 1:1.15)

in the presence of 80 ppm of test substance. At room temperature, by means of a scattered-light photometer, the course of turbidity was then followed and assessed.

The assessment was done by the following grading scale:

grade 4 (poor) = blind specimen

3 (mediocre) = marked lessening in the level of turbidity compared with the blind value

2 (good) = occurrence of turbidity after a pronounced delay, or severely reduced turbidity

1 (very good) = no turbidity within 45 minutes

The results are shown in Table I.

Example 6: Wash test

Various test fabrics (terry cloth, EMPA cotton [EMPA = Eidgenössische Materialprüfungsanstalt, St. Gallen, Switzerland], WFK cotton [WFK = Wäschereiforschung Krefeld, Germany], WFK polyester-cotton, 2/2 rib) were washed 20 times at 93°C and 18° d with a test detergent A of the following composition (dosage per 150 g in pre-wash and main wash).

A:	weight %
NTPP	22.0
Alkyl benzene sulfonate	7.0
Nonionic surfactants	4.0
Soap	3.5
Carboxymethylcellulose	1.5
Ethylenediaminetetraacetate (EDTA)	0.2
Optical brightener	0.2
Enzymes	0.25
$NaBO_3 \cdot 4H_2O$	20.0
Sodium disilicate	5.0
Magnesium silicate	2.0
Na_2SO_4	34.35

Next, the inorganic fabric incrustation was ascertained by incineration at 800°C:

By repeating the test with the addition of 1 weight % of copolymer acrylic acid/1-phenylvinyl-1-phosphonic acid (ACS/PVP; molar ratio 10:1), referred to the quantity of detergent, it was possible to lower the inorganic fabric incrustation markedly (Table II).

Example 7: Wash test

EMPA cotton as in Example 6 was washed 25 times at 60°C and 18° d with a test detergent B of the following composition (dosage 160 g, main wash only:

B:	weight %
NTPP	25.0
Zeolite A	15.0
Soda	1.7
Sodium perborate tetrahydrate	22.0
Anionic surfactants	8.4
Nonionic surfactants	3.6
Soaps	3.8

The inorganic fabric incrustation was ascertained by incineration at 800°C. The test was repeated in the presence of 1.6 weight % of copolymer in accordance with Example 2, referred to the quantity of detergent, by which virtually the same reduction in fabric incrustation was attained as by the addition of 3.1 weight % of sodium nitrilotriacetate (NTA) (Table II).

Example 8: Wash test

An even better result was attained with test detergent B by adding 1.6 weight % of copolymer acrylic acid-1-phenylvinyl-1-phosphonic acid (ACS/PVP; molar ratio 10:1) (Table II).

Table I

Monomer a	Monomer b	Molar ratio a : b	Example 3 Calcium binding capacity (mg Ca/g Na-salt) 20°C	60°C	Example 4 Dispersion test Grade	Example 5 Threshold test Grade
$CH_2=CHCOOH$	$H_2C=C(C_6H_5)PO_3H_2$	10 : 1	250	250	1	1
		5 : 1 Example 1	294	294	1	1
$CH_2=CHCOOH$	$H_2C=C(CH_3)PO_3H_2$	10 : 1 Example 2	184	146	1	2
		3 : 1	202	202	1	1
For comparison: $Na_5P_3O_{10}$ (NTPP)			130	130	2	1
$Na(CH_2COONa)_3$			194	170	3-4	4
Zeolite A			114 a)			

a) Manufacturer indication, back titration with EDTA after filtration

Table II

Weight % of ash after 20 washing cycles

Product	Terry cloth	EMPA cotton	WFK cotton	WFK polyester-cotton	2/2 Rib
A	3.18	2.68	1.78	1.10	2.98
A + 1 Weight % ACS/PVP	1.57	2.30	1.40	0.33	1.43

Weight % of ash after 25 washing cycles

Product	EMPA cotton
B	8.3
B + 3,1 Weight % NTA	5.9
B + 1,6 Weight % ACS/PVP (10:1)	5.9
B + 1,6 Weight % ACS/ propenephosphonic acid (10:1)	6.1

Claims:

1. A washing and cleaning agent, having 5 to 70 weight % of at least one surfactant, 0.1 to 50 weight % of at least one builder, and conventional washing adjuvants, characterized by the following builder contents:

a) 0.1 to 25 weight % of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

aa) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

bb) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

cc) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.

b) 0 to 49.9 weight % conventional builders.

2. The use as a builder or builder additive, in washing and cleaning agents, of a copolymer, which can be obtained by copolymerization, known per se, of the following monomers:

a) 40 to 99.9 Mol % of ethylenically unsaturated carboxylic acids or their alkali salts having the general formula $R^1(R^2)C = C(R^3)COOX$,

in which X stands for H, alkali metal;

R^2 stands for H, COOX, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^1, R^3 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

or anhydrides thereof;

b) 0.1 to 40 Mol % of ethylenically unsaturated phosphonic acids or their alkali salts having the general formula $R^4(R^5)C = C(R^6)PO_3X_2$,

in which X stands for H, alkali metal;

R^4, R^5 stand for H, C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

R^6 stands for C_1 to C_4 alkyl, C_5 to C_8 cycloalkyl, phenyl, or substituted phenyl;

c) 0 to 20 Mol % olefinically unsaturated compounds without carboxylic or phosphonic acid groups.